

Localization of a multiblock copolymer at a selective interface: Scaling predictions and Monte Carlo verification

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Abstract

We investigate the localization of a hydrophobic - polar (HP) - regular copolymer at a selective solvent-solvent interface with emphasis on the impact of block length M on the copolymer behavior. The considerations are based on simple scaling arguments and use the mapping of the problem onto a homopolymer adsorption problem. The resulting scaling relations treat the gyration radius of the copolymer chain perpendicular and parallel to the interface in terms of chain length N and block size M , as well as the selectivity parameter χ . The scaling relations differ for the case of weak and strong localization. In the strong localization limit a scaling relation for the lateral diffusion coefficient $D_{||}$ is also derived. We implement a dynamic off-lattice Monte - Carlo model to verify these scaling predictions. For chain lengths in a wide range ($32 \leq N \leq 512$) we find good agreement with the scaling predictions.

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I. INTRODUCTION

The behavior of hydrophobic - polar copolymers (or HP - copolymer) at a selective interface (the interface which divides two immiscible liquids, say, water and oil, each of them being good for one type of monomers and bad for the other) is of great importance in the chemical physics of polymers. HP - copolymers are readily localized at such an interface because under a sufficiently large degree of selectivity the hydrophobic and polar parts of a copolymer chain try to stay on different sides of the interface due to the interplay between the entropy loss in the vicinity of the interface and the energy gain in the proper solvent. This reduces the interfacial tension between the immiscible liquids and motivates the main practical use of such copolymers as compatibilizers¹. Early in the study of compatibilizers, the attention has been focused mainly on diblock copolymers due to their relatively simple structural characteristics^{2,3}. These studies of diblock compatibilizers have been extended later by making use of the numerical self - consistent field approach and of Monte Carlo (MC) simulations^{4,5,6,7,8}. The seminal paper by Garel et. al.⁹ has attracted attention to the interface localization of *random* HP - copolymer and has brought about a great number of publications on this subject^{10,11,12,13,14,15,16,17,18,19}. As a rule, the macromolecules considered in these studies pertain to random or strictly alternating copolymers whereas the impact of block size on the localization transition and on the properties of the interface have found comparatively little attention. In fact, to the best of our knowledge the only MC - simulation of multiblock HP - copolymers at a selective interface has been carried out by Balasz et al.²⁰ within a two-dimensional model where no treatment in terms of scaling has been suggested.

In this paper we focus on the interesting special case of multiblock copolymers made of a regular sequence of HP - diblocks where the fractions of H - and P - segments are equal. The main objective is to bring together simple scaling arguments and the findings of MC - simulations. The principal idea of the scaling consideration in this case implies (see ref.^{21,22,23}) that the problem at hand can be mapped onto the homopolymer adsorption problem whereby each HP - diblock (e.g. each part of consecutive blocks made of H- and P-monomers, respectively) acts as an *effective* segment. At the interface these HP - diblocks behave as “soft dipoles” so that their “polarization” minimizes the free energy. This phenomenon governs the HP - diblock effective attraction energy, and enables the mapping onto the problem of a homopolymer adsorption at a penetrable surface^{24,25}.

In Sec.II we provide refined scaling considerations which are partially based on previous results^{14,21,23}. The results are presented in such a form that the chain and block length dependences are clearly separated and can be easily compared with the MC - findings. In Sec. III we report on the results of a comprehensive MC - simulation study and compare these results with the scaling predictions. We conclude with a brief summary and an outlook for further work.

II. SCALING

A. Static

As mentioned before, the scaling treatment is based on the idea that a regular multiblock copolymer can be considered as a homopolymer where a single HP - diblock plays the role of an effective segment. All such diblocks try to keep their H - and P - segments in the corresponding preferable environment. This leads to the diblock “polarization” at the interface and to a free energy gain which produces an effective attraction energy E . We restrict ourselves here to the fully symmetric case. This means that the energy gain χ (which is the selectivity parameter) for a P - monomer in its own (polar) environment is equal to the corresponding energy gain for a H - monomer, provided the latter stays in the hydrophobic environment. Also, the P - and H - parts of a diblock have an equal number of monomers. An estimate for the effective attraction energy per diblock of length $2M$ (M being the number of monomers of each species in the diblock) then reads^{21,22}.

$$E \sim -\chi^2 M^2, \quad (1)$$

where we measure the energy in units of $k_B T$, (i.e. $\chi/k_B T \rightarrow \chi$ is dimensionless) where k_B denotes the Boltzmann constant.

Now consider a multiblock copolymer of length N which consists of $\mathcal{N} = N/2M$ diblocks. At the adsorption threshold, χ_c , the attraction energy per chain scales as²⁵ $V_{\text{attr}} \approx |E|\mathcal{N}^\phi$, where ϕ denotes the so called crossover exponent. It has been shown rigorously²⁶ that the relation $\phi = 1 - \nu$ (here $\nu = 0.6$ is the Flory exponent in 3D space) is correct for the case of a penetrable surface. At χ_c the attractive energy, $V_{\text{attr}} = V_{\text{attr}}^c$, should be of the order of the thermal energy, i.e.

$$|E^c|\mathcal{N}^{1-\nu} \approx 1. \quad (2)$$

Taking into account eq. (1), the expression for the critical selectivity then yields

$$\chi_c \sim M^{-(1+\nu)/2} N^{-(1-\nu)/2}. \quad (3)$$

Eq.(2) refers to the chain as a whole at the localization threshold χ_c . As the selectivity parameter χ increases, each part of the chain (named "blob") containing g monomers accumulates an energy of the order of $k_B T$. Note that the chain "neutrality" requires that g/M is always an even number. The blob length g may be determined from $|E|(g/M)^{1-\nu} \approx 1$, so that

$$g \sim \chi^{-2/(1-\nu)} M^{-(1+\nu)/(1-\nu)}. \quad (4)$$

The localized chain as a whole can be considered as a string of such blobs.

It is customary²⁷ to take the number of blobs, $N/g \sim \chi^{2/(1-\nu)} M^{(1+\nu)/(1-\nu)} N$ as a natural scaling variable in the various scaling relations. For the sake of convenience, we take this variable in the following form

$$\eta \equiv \chi M^{(1+\nu)/2} N^{(1-\nu)/2}. \quad (5)$$

Then the chain size perpendicular to the interface direction scales as

$$R_{g\perp} = l N^\nu \mathcal{G}(\eta) \quad , \quad (6)$$

where l is the Kuhn segment and $\mathcal{G}(\eta)$ is some scaling function.

One should discriminate between the cases of weak and strong localization²³. In the weak localization regime the scaling argument η is of the order of one (cf. eq.(3)), and the scaling function $\mathcal{G}(\eta)$ has a power law behavior, i.e.

$$\mathcal{G}(\eta) = \begin{cases} 1 & , \text{ at } \eta < 1 \\ \eta^\alpha & , \text{ at } \eta \geq 1 \end{cases} \quad , \quad (7)$$

where $\alpha = -2\nu/(1-\nu)$. This value of the exponent α has been found from the condition that at $\eta \geq 1$ the value of $R_{g\perp}$ is determined by the blob size alone, i.e. it does not depend on N .

Similar reasoning can be used for the chain size in direction parallel to the interface $R_{g\parallel}$, namely

$$R_{g\parallel} = l N^\nu \mathcal{H}(\eta) \quad , \quad (8)$$

where $\mathcal{H}(\eta)$ is some scaling function. Again, the form of $\mathcal{H}(\eta)$ can be determined by the condition that at $\eta \geq 1$ the localized multiblock chain behaves as a two - dimensional self - avoiding string of blobs, i.e. $R_{||} \sim N^{\nu_2}$, where $\nu_2 = 0.75$ is the Flory exponent in $2d$ space. As a result one finds

$$\mathcal{H}(\eta) = \begin{cases} 1 & , \text{ at } \eta < 1 \\ \eta^\beta & , \text{ at } \eta \geq 1 \end{cases} , \quad (9)$$

where $\beta = 2(\nu_2 - \nu)/(1 - \nu)$.

As the selectivity parameter χ grows further, a characteristic point $\chi = \chi_\infty$ can be reached where $R_{g\perp}$ and $R_{g||}$ approach a plateau and do not change any further. This is the strong localization limit where the number of monomers in the blob becomes of the order of the block length, i.e. $g \approx M$. By making use of this condition in eq. (4) we can write for the characteristic selectivity χ_∞ the following simple relation

$$\chi_\infty \sim M^{-1}. \quad (10)$$

which corresponds to the well known Flory-Huggins limit of phase separation. Note that χ_∞ depends only on the block size M and does not depend on the chain length N . Given this value one can go back to eqs.(6 - 9) and check the scaling in the strong localization limit. The resulting relations are

$$R_{g\perp} = lM^\nu, \quad (11)$$

$$R_{g||} = lM^\nu \left(\frac{N}{M} \right)^{\nu_2} \sim M^{-(\nu_2 - \nu)} N^{\nu_2}. \quad (12)$$

which reflect the pancake geometry of a polymer localized at the surface. The relations (11) and (12) can be expected because in this regime all P - and H - segments are predominantly in their preferred solvents. In addition, the scaling estimate of the polymer size perpendicular to the interface shows that the perpendicular extension of the chain is entirely determined by the size of the blob.

The free energy gain in the localized state is proportional to the number of blobs²⁷, i.e.

$$F_{\text{loc}} \sim \frac{N}{g} \sim \chi^{2/(1-\nu)} N M^{(1+\nu)/(1-\nu)} , \quad (13)$$

where eq.(4) has been used. In terms of η eq.(13) reads

$$F_{\text{loc}} = \eta^{2/(1-\nu)} \quad \text{at} \quad 1 \leq \eta \leq \eta_\infty, \quad (14)$$

where $\eta_\infty = \chi_\infty M^{(1+\nu)/2} N^{(1-\nu)/2} \sim (N/M)^{(1-\nu)/2}$. At $\chi > \chi_\infty$ the free energy gain follows the strong localization law

$$F_{\text{loc}} \sim \chi N \quad , \quad (15)$$

which is mainly triggered by the energy gain.

B. Dynamics

After the localization on the selective interface, the multiblock copolymer can only diffuse in the two - dimensional space along the surface. Here we give the scaling estimate for the characteristic time τ which is necessary for a chain to displace along the surface a distance equal to its own gyration radius. We define this time in terms of the chain length N and the block length M in the strong localization limit.

The diffusion coefficient of the whole chain along the surface can be estimated as

$$D_{\parallel} \approx \left(\frac{1}{\zeta} \right) \frac{1}{\mathcal{N}} = \frac{D_{\text{block}}}{\mathcal{N}}, \quad (16)$$

where D_{block} is the diffusion coefficient of one block, $\zeta = \zeta_0 M$ the corresponding friction coefficient and the number of diblocks $\mathcal{N} = N/2M$. The characteristic time of the 2 - dimensional chain displacement obeys

$$\tau \approx \frac{R_{\text{block}}^2 \mathcal{N}^{2\nu_2}}{\left(\frac{1}{\zeta} \right) \frac{1}{\mathcal{N}}}, \quad (17)$$

where the characteristic size of the block (which spreads in the 3 - dimensional space) $R_{\text{block}} \approx l M^\nu$ ($\nu = 0.6$) whereas the 2 - dimensional Flory exponent is $\nu_2 = 0.75$.

Now one can express all quantities in eq.(17) in terms of N and M . As a result one obtains

$$\begin{aligned} \tau &\approx \zeta_0 l^2 M^{2(\nu-\nu_2)} N^{2\nu_2+1} \\ &\approx \zeta_0 l^2 M^{-0.3} N^{2.5}. \end{aligned} \quad (18)$$

It is clear that this result should hold for sufficiently long chains and blocks.

III. MC - SIMULATION

A. Description of the model

The off-lattice bead-spring model has been used previously for simulations of polymers both in the bulk^{28,29} and near confining surfaces^{30,31,32,33,34,35}; thus, we describe here the salient features only. Each polymer chain contains N effective monomers connected by anharmonic springs described by the finitely extendible nonlinear elastic (FENE) potential.

$$U_{FENE} = -\frac{K}{2}R^2 \ln \left[1 - \frac{(\ell - \ell_0)^2}{R^2} \right]. \quad (19)$$

Here ℓ is the length of an effective bond, which can vary in between $\ell_{min} < \ell < \ell_{max}$, with $\ell_{min} = 0.4$, $\ell_{max} = 1$ being the unit of length, and has the equilibrium value $\ell_0 = 0.7$, while $R = \ell_{max} - \ell_0 = \ell_0 - \ell_{min} = 0.3$, and the spring constant K is taken as $K/k_B T = 40$. The nonbonded interactions between the effective monomers are described by the Morse potential

$$U_M = \epsilon_M \{ \exp[-2\alpha(r - r_{min})] - 2 \exp[-\alpha(r - r_{min})] \}, \quad (20)$$

where r is the distance between the beads, and the parameters are chosen as $r_{min} = 0.8$, $\epsilon_M = 1$, and $\alpha = 24$. Owing to the large value of the latter constant, $U_M(r)$ decays to zero very rapidly for $r > r_{min}$, and is completely negligible for distances larger than unity. This choice of parameters is useful from a computational point of view, since it allows the use of a very efficient link-cell algorithm³⁶. From a physical point of view, these potentials eqs. (19), (20) make sense when one interprets the effective bonds as kind of Kuhn segments, comprising a number of chemical monomers along the chain, and thus the length unit $\ell_{max} = 1$ corresponds physically rather to 1 nm than to the length of a covalent $C - C$ bond (which would only be about 1.5Å). Since in the present study we are concerned with the localization of a copolymer at good solvent conditions, in eq.(20) we retain the repulsive branch of the Morse potential only by setting $U_M(r) = 0$ for $r > r_{min}$ and shifting $U_M(r)$ up by ϵ_M .

The interface potential is taken simply as a step function with amplitude χ ,

$$U_{int}(n, z) = \begin{cases} -\sigma(n)\chi/2, & z > 0 \\ \sigma(n)\chi/2, & z \leq 0 \end{cases} \quad (21)$$

where the interface plane is fixed at $z = 0$, and $\sigma(n) = \pm 1$ denotes a "spin" variable which distinguishes between P- and H- monomers. The energy gain of each chain segment is thus $-\chi$, provided it stays in its preferred solvent.

Two typical snapshots for a chain with $N = 128$ and $M = 8$ in the weak ($\chi = 0.25$) and strong ($\chi = 10$) localization limits are shown in Fig.1 to illustrate the main features of the model.

In each Monte Carlo update, a monomer is chosen at random and one attempts to displace it randomly by displacements Δx , Δy , Δz chosen uniformly from the intervals $-0.5 \leq \Delta x, \Delta y, \Delta z \leq 0.5$. The transition probability for such an attempted move is simply calculated from the total change ΔE of the potential energies defined in eqs. (19 - 21) as $W = \exp(-\Delta E/k_B T)$. According to the standard Metropolis algorithm, the attempted move is accepted only if W exceeds a random number uniformly distributed between zero and unity. Since our potentials are constructed such that chains cannot intersect themselves in the course of random displacement of beads, one does need to check separately for entanglement restrictions. In the course of the simulation the starting configuration of the copolymer is relaxed for a period of time τ_0 before measurements of the chain properties are carried out. We sample various static and dynamic quantities as the components of the gyration radius perpendicular, $R_{g\perp}$, and parallel, $R_{g\parallel}$, to the interface, the density distribution of the two kinds of monomers around the interface, internal energy, specific heat, diffusion coefficients, etc. We use periodic boundary conditions in the plane of the interface while there are rigid walls in the z - direction, where the simulation box extends from $z = -16$ to $z = 16$. The algorithm is reasonably fast, i.e. one performs $\approx 0.5 \times 10^6$ updates per CPU second on a 2.8 GHz PC. Typically we studied chains with length $32 \leq N \leq 512$ and all measurements have been averaged over 2^{17} samples.

B. Results

The localization at the selective interface can be considered as a phase transition at least in the limits: $N \rightarrow \infty$, $M \rightarrow \infty$ and $\chi \rightarrow 0$ with $\eta_c \equiv \chi_c N^{(1-\nu)/2} M^{(1+\nu)/2} = 1$. At finite N, M and χ the transition looks like a smooth crossover and one can define an order parameter (OP) in terms of the fractions of P - and H - monomers in the polar (at $z > 0$) and hydrophobic (at $z < 0$) semispace, respectively, i.e.

$$\text{OP} = \sqrt{f_P^> f_H^<} \quad (22)$$

Fig.2 shows the variation of this OP with the selectivity parameter χ for a chain length $N = 128$ and various lengths of the blocks M . Evidently, for sufficiently large M the OP reaches saturation at much lower values of χ than for short blocks. It can also be seen that the chains with small M even in the localized state display a much lower degree of ordering than those with longer blocks since in the localized phase the number of "frustrated" monomers which stay in the wrong solvent increases with vanishing proximity to the interface.

The transition location, χ_c , defined as the inflection point of the curves in Fig. 2 can be easily calculated. A more comprehensive information about the localization is revealed from the monomer density distribution histogram which is given in Fig. 3. While for $\chi = 0.25$ the copolymer is still not localized, even at $\chi = 0.75 > \chi_c$ there is still a considerable amount of segments which stay in the wrong solvent and one needs a rather strong segregation $\chi = 5.0$ in order to keep the segments entirely in their preferred environment.

The localization at the interface is also marked by a maximum in the specific heat of the system - $C_v(\chi) = (Nk_b T^2)^{-1} (\langle E^2 \rangle - \langle E \rangle^2)$ - which we obtain from the fluctuations of the internal energy of the copolymer E and show in Fig. 4. One can readily see from Fig. 4 that the specific heat curves collapse (despite significantly larger scatter in the measured data) onto different master curves for the two block sizes in concern. However, the heights of the C_v -maxima at the localization transition appear rather insensitive with respect to chain length N . Indeed, it has been shown earlier³⁷ that the specific heat critical exponent is zero, and there exist only weak logarithmic corrections to finite size scaling ($C_v \sim (\ln N)^{3/11}$ for a Gaussian chain). One can also infer from Fig. 4 a rapid decrease in the height of the C_v -maximum with growing block size M which is to be expected bearing in mind that the chance for an energy fluctuation rapidly diminish as less and less monomers cross into the "wrong" solvent with increasing M .

1. Weak localization

We turn now to the comparison of our data with the scaling prediction given in Sec.II. Figure 5 displays the variation of the chain size perpendicular to the interface $R_{g\perp}$ with scaling parameter η . One can easily distinguish between the cases of weak and strong localization. In the first case the curves collapse nicely on a master curve in a range of η which gets narrower with growing M . This proves the scaling law given by eq. (7) and is also in line with the trend given by eq. (10) for the characteristic selectivity χ_∞ at the onset of the strong localization regime. The scaling function, eq. (7), is characterized by the exponent $\alpha = -3$, which is indicated by the dashed line in Fig. 5 and appears in good agreement with the simulation data. An interesting case which we observe in all our studies is shown in the inset of Fig. 5 - in the case of a *diblock* (i.e. when $M = N/2$) in the strong localization regime one finds $R_{g\perp}(\eta)/R_{g\perp}(0) \geq 1$. Clearly, as the two blocks tend to stay away from the interface, thus maximizing entropy, they induce an elongation of the coil perpendicular to the interface in contrast to the behavior of multiblock copolymers.

The set of graphs shown in Fig. 5 has been used to evaluate the critical χ_c taken as the positions of the respective inflection points. The result of this evaluation is shown in Fig. 6. The insert shows the M - dependence of χ_c at different N . Evidently, the rescaling according to eq. (3) leads to the master curve. The dashed line demonstrates the scaling prediction $\chi_c \sim M^{-0.8}$ and is again in a good agreement with theory. Not surprisingly, at small M one observes deviations from the expected power-law behavior which demonstrate that scaling validity is achieved in the asymptotic limit only.

Similar scaling representation has been done also for the parallel component of the chain size $R_{g\parallel}$ (see Fig. 7). In the weak localization regime all data collapse again into a master curve. The scaling exponent $\beta = 3/4$ (noted by the dashed line, see eq.(9) is fairly close to the simulational results.

2. Strong localization

The area where $R_{g\perp}$ and $R_{g\parallel}$ abandon the master curves in Figs. 5, 7 and approach different plateau values at high η corresponds to the strong localization regime. In this case the scaling should follow eqs. (11) and (12). We have evaluated $R_{g\perp}(\infty)$ from the plateau

height values in Fig. 5 (dropping out the factor $1/R_{g\perp}(0)$). The corresponding results are shown in Fig. 8. The M - dependence of $R_{g\perp}(\infty)/l$ is given for different chain lengths N . The finite size analysis indicates that an extrapolation to $1/N \rightarrow 0$ leads to the correct Flory scaling $R_{g\perp}(\infty) \sim M^{0.6}$ (see the dashed line in Fig. 8). Fig. 9 makes it also apparent that the parallel component $R_{g\parallel}(\infty)$ follows to a good accuracy the law $R_{g\parallel}(\infty)/l \sim M^{-0.15} N^{0.75}$ which comes from eq. (12). Thus Fig. 9 demonstrates as well the scaling relation for the relaxation time τ given by eq.(17). The fit of our MC - results with the theoretical scaling prediction $\tau \sim M^{-0.3} N^{2.5}$ is very good especially taking into account the relatively small values of the block length.

IV. CONCLUSION AND OUTLOOK

In the preset work we have studied the adsorption of regular HP copolymer at a penetrable interface between two immiscible fluids. Specifically, we have focused our attention on the influence of the block size M on the adsorption transition as it is known that efficient compatibilizing agents (i) reduce the surface tension and (ii) enhance the adhesion between the surfaces that result upon cooling. While reduced surface tension is achieved by possibly higher surface coverage by the polymer, for enhanced adhesion between the components each block should extend and penetrate a significant distance into the respective compatible melt. Qualitatively it is clear that shorter blocks will provide a more efficient reduction of the surface tension whereas longer blocks would favor better adhesion between the segregated systems. In order to get more quantitative insight into the effectiveness of multiblock copolymers we develop a simple scaling treatment which is then compared against simulational results.

Within the framework of our simple scaling approach we arrive at several important conclusions characterizing the impact of block length M on the behavior of regular multiblock copolymers at a fluid-fluid interface:

- The critical selectivity decreases with growing block length as $\chi_c \sim M^{-(1+\nu)/2}$ while the crossover selectivity to the strong localization regime vanishes as $\chi_\infty \sim M^{-1}$.
- The size of the copolymer varies in the weak localization regime as $R_{g\perp} \sim M^{-\nu(1+\nu)/(1-\nu)}$ and $R_{g\parallel} \sim M^{(\nu_2-\nu)(1+\nu)/(1-\nu)}$.

- In the case of strong segregation we obtain respectively $R_{g\perp} \sim M^\nu$ and $R_{g\parallel} \sim M^{-(\nu_2-\nu)}$.
- The typical relaxation time in the case of strong localization varies as $\tau \sim M^{2(\nu-\nu_2)}$ with block length.

Our computer experiments appear to confirm nicely these predictions.

Concluding, one should point out that this study has been focused on one aspect of the localization of copolymers at penetrable interfaces. A number of related topics such as the case of many chains in the system, the presence of attractive interactions between similar segments, or the kinetics of localization could provide further valuable insights on the problem. Another interesting aspect comes when random - or specifically sequenced copolymers are considered rather than regular multiblock copolymers. In these cases additional information is stored in the sequence of the H and P monomers. The relevant information can be read by the interfacial behavior of such polymers. Indeed, the localization will then depend on the distribution of the H and P monomers along the chain. For special sequences we expect to relate their behavior to some typical proteins³⁸. We hope to be able to report on some of these topics in the near future.

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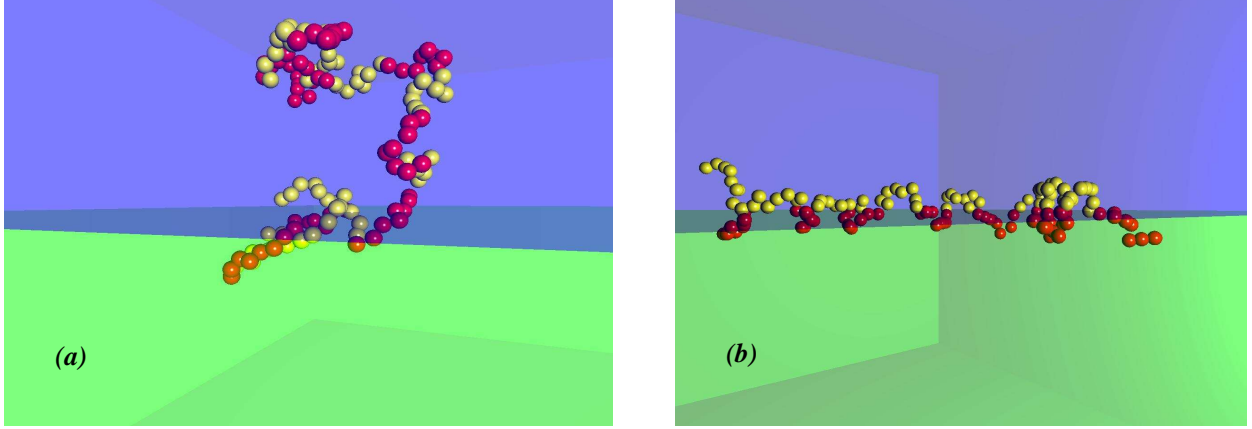


FIG. 1: Snapshots of typical configurations of a copolymer with $N = 128$, $M = 8$ at $\chi = 0.25$ (a), and $\chi = 10$ (b). The value of the critical selectivity for this chain is $\chi_c = 0.67$.

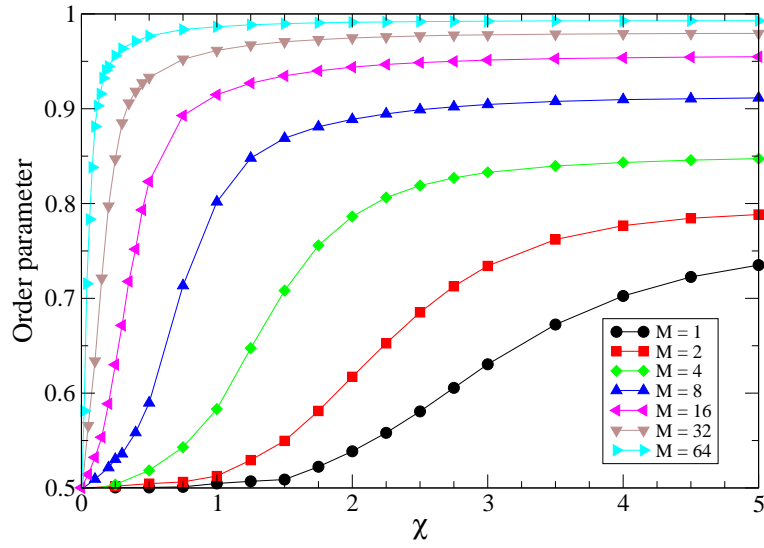


FIG. 2: The order parameter for chain length $N = 128$ vs selectivity χ for different values of the block length M .

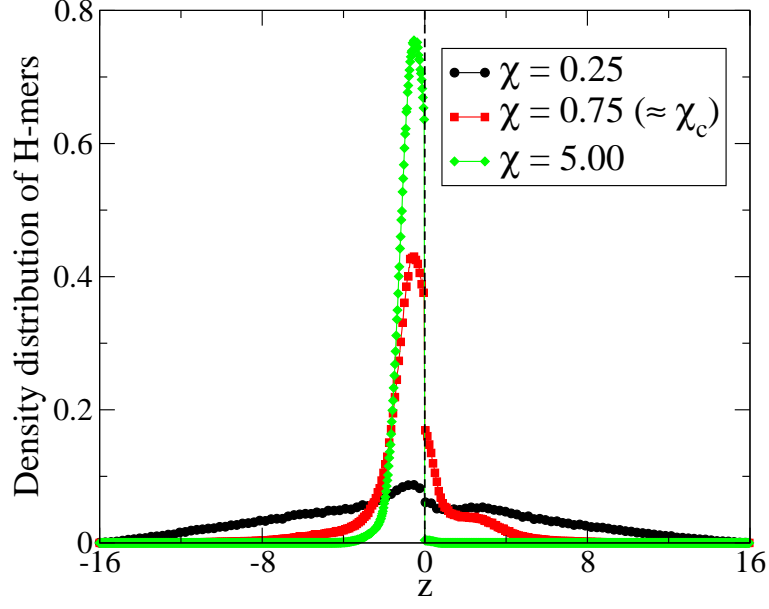


FIG. 3: Density distribution of the H - monomers for a chain with $N = 128$ and $M = 8$ at three different values of χ . The critical selectivity is $\chi_c \approx 0.67$.

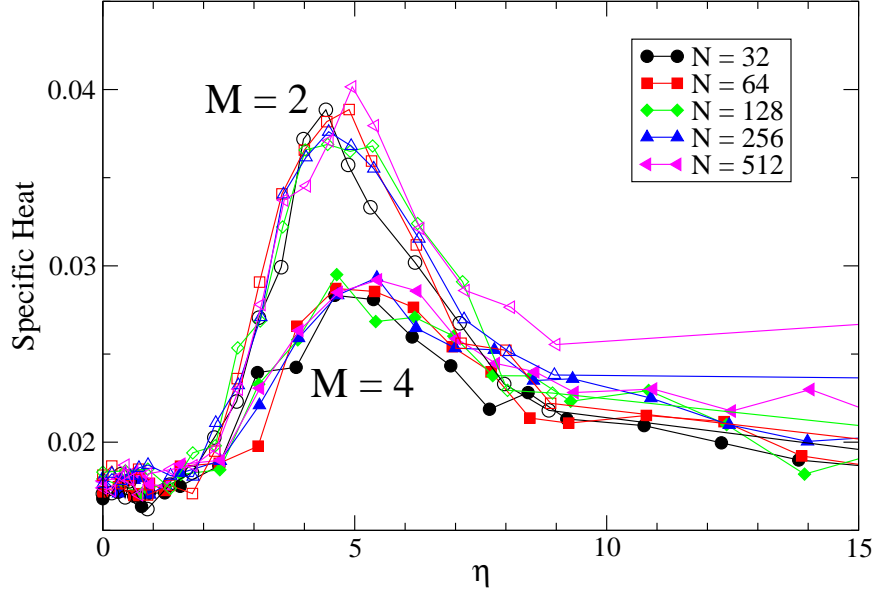


FIG. 4: Specific heat (per monomer) of a copolymer chain with length $32 \leq N \leq 512$ and two block sizes $M = 2, 4$ at the localization transition.

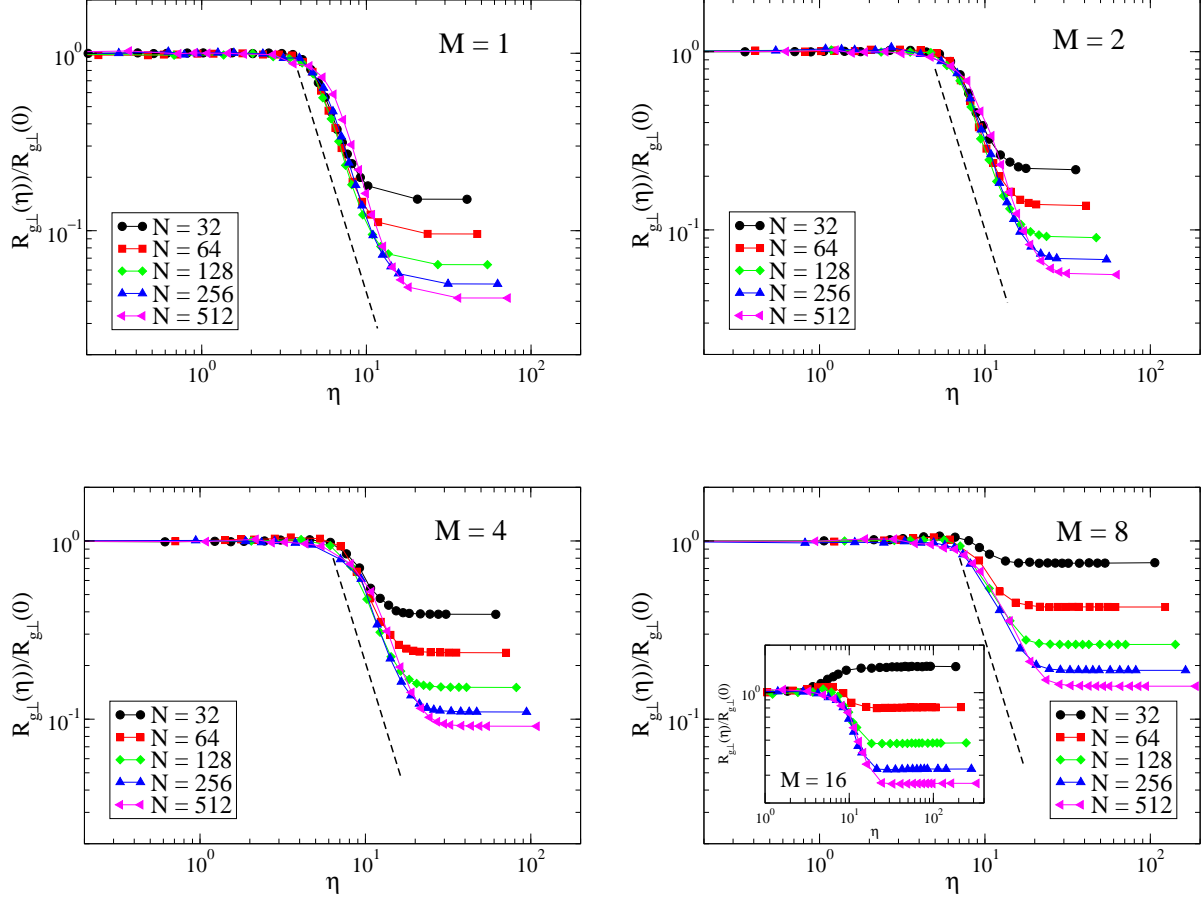


FIG. 5: Variation of the chain size perpendicular to the interface $R_{g\perp}$ with the scaling variable η for block lengths $M = 1, 2, 4, 8$ and 16 (inset). In all cases the dashed line indicates the scaling prediction.

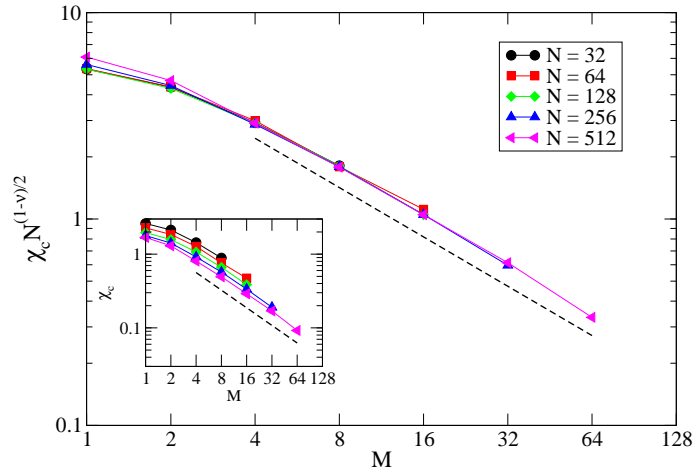


FIG. 6: Scaling plot of the critical selectivity χ_c in terms of block length M and chain length N . The dashed line indicates the scaling prediction. The inset shows χ_c vs M without scaling in N .

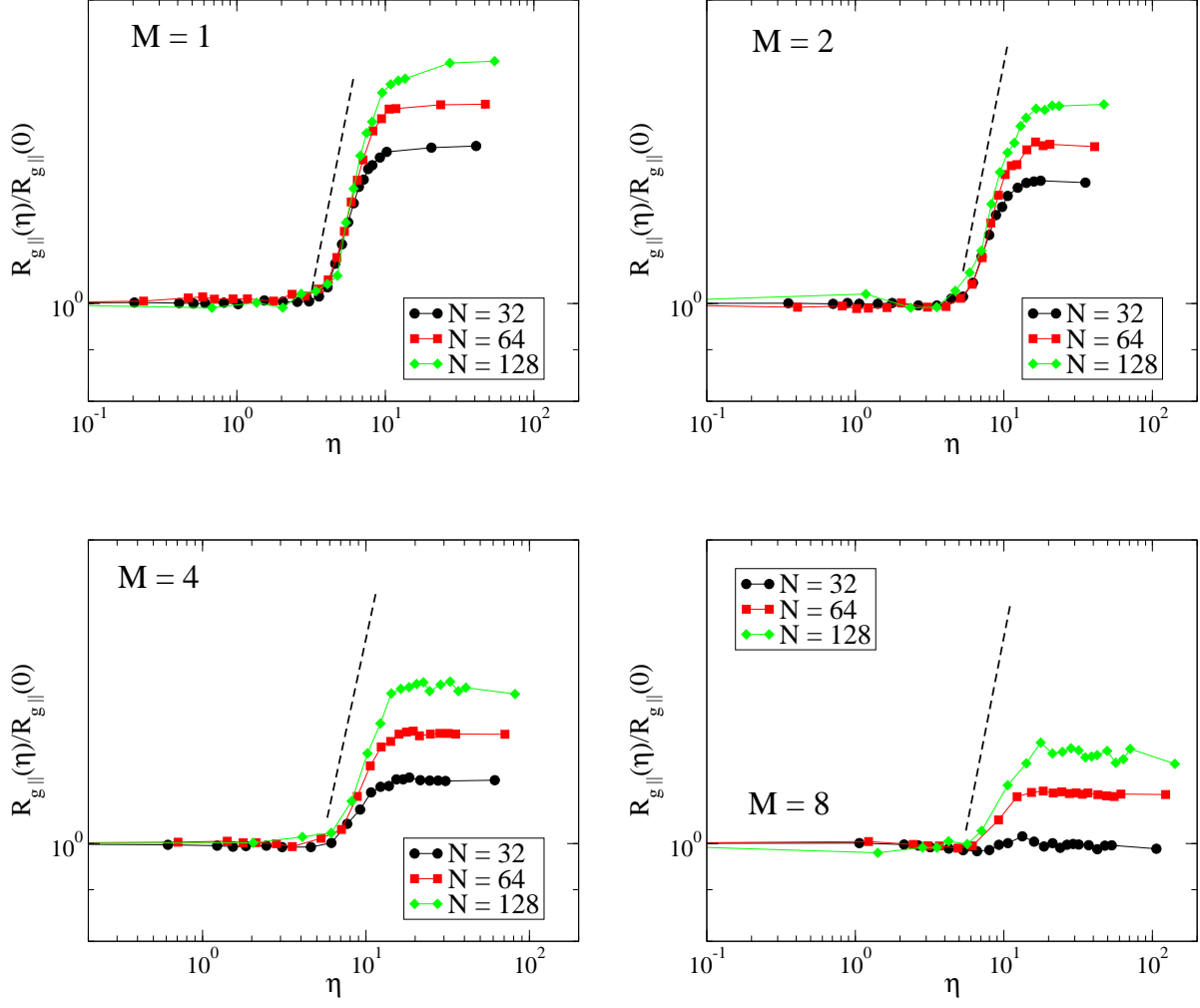


FIG. 7: Variation of $R_{g||}$ with the scaling variable η for chain lengths $32 \leq N \leq 512$ and several block lengths, as indicated. The onset of the strong localization regime is manifested by the decay of the master curves into different curves for each N . In all cases the dashed line indicates the scaling prediction.

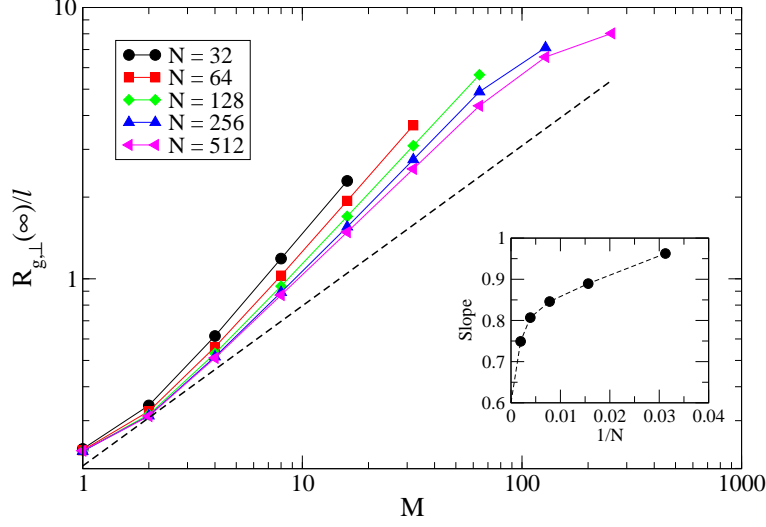


FIG. 8: The perpendicular component $R_{g\perp}(\infty)/l$ as a function of M at the different N . The dashed line corresponds to the scaling prediction. The insert shows the extrapolation for $1/N \rightarrow 0$ as leading to the theoretical value of the slope $\nu = 0.6$.

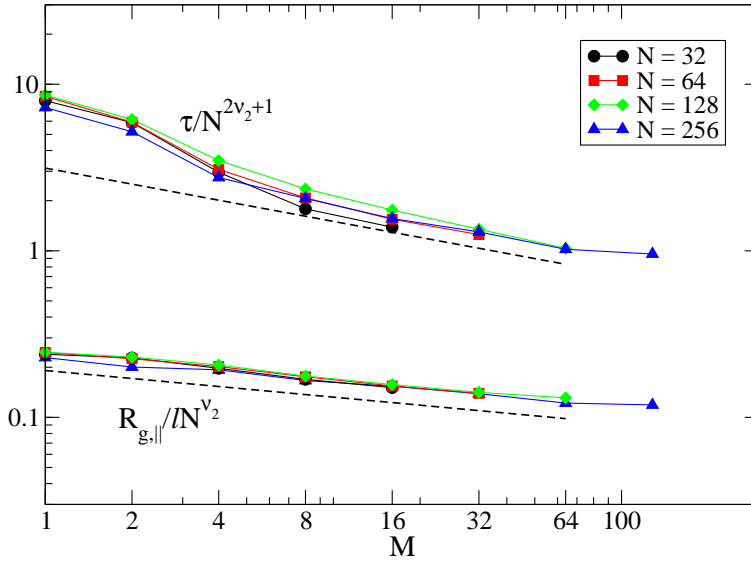


FIG. 9: The upper curve represents the rescaling of the characteristic time τ according to eq. (17). The lower curve shows that the scaling for $R_{g\parallel}(\infty)$ follows eq.(12). The dashed lines indicate the scaling predictions.